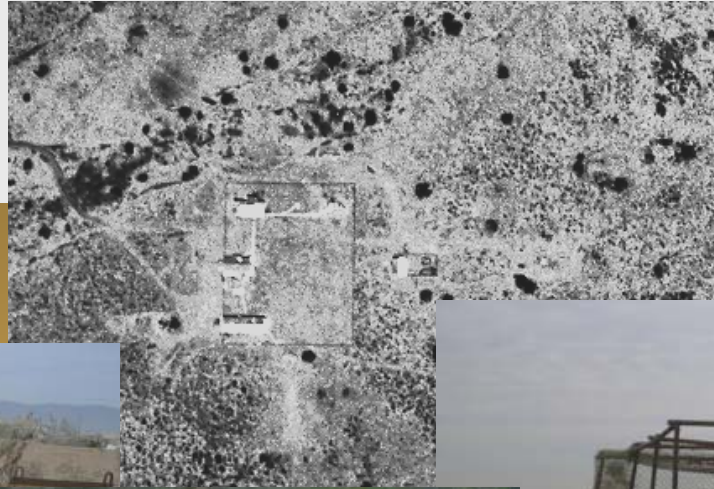


Perchlorate, TCE, and Dioxane Investigation and Remediation in a Semiarid Environment

Presentation by:
Ted Tyler
Dave Jenkins



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INTRODUCTION

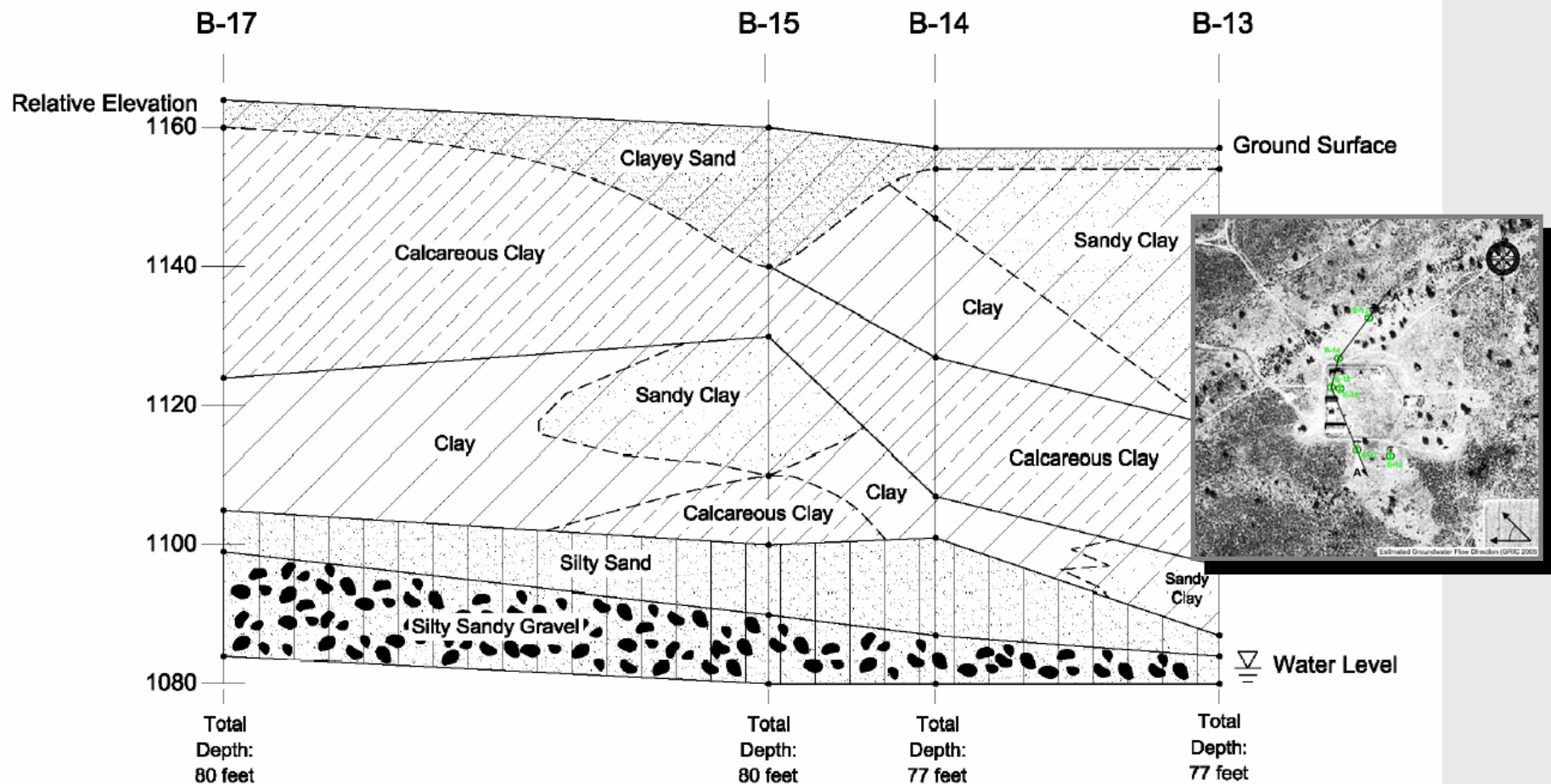
- Site Description
- Site Conceptual Model Development
- Remedial Approach
- Related Case Studies (Dave Jenkins)

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HYDROGEOLOGIC ENVIRONMENT



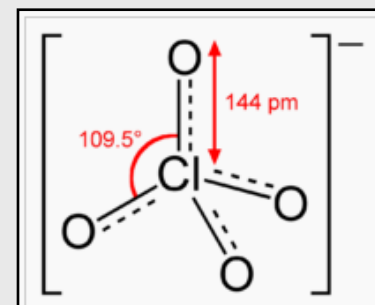
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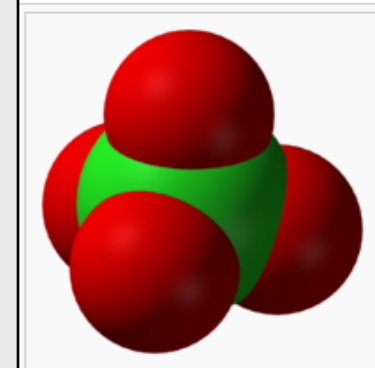
CHEMICAL PROPERTIES

Perchlorate

- Ammonium perchlorate is used as an oxidizer in solid rocket propellant
- Low volatility
- *Adsorbs weakly to most soil minerals (NO_3^- and Cl^- more favorable)*
- *Will accumulate in low permeability zones*
- Density (concentrated solutions will sink Ammonium perchlorate: SG = 1.95)
- High solubility and mobility
 - *Ammonium Perchlorate 245,000 mg/l @ 25°C*
- *Biodegradability: Limited Natural Biological Reduction*
- *EPA Reg. IX Soil PRG 7.8 mg/kg (res); 100 mg/kg (ind)*
- *California effective Oct. 18, 2007; MCL = 6 ppb (GW)*



The structure and dimensions of the perchlorate ion



A space-filling model of the perchlorate ion

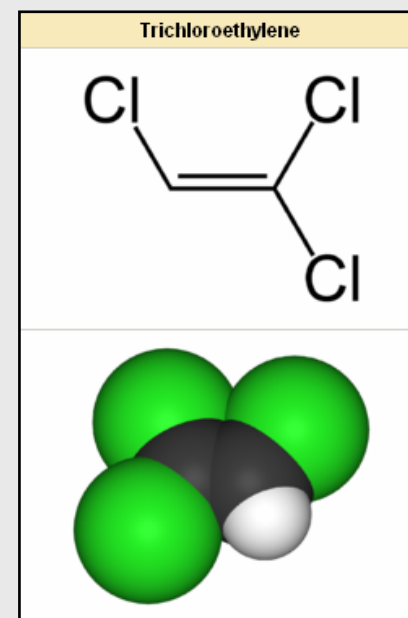
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CHEMICAL PROPERTIES

Trichloroethylene (TCE)

- Vapor Pressure 69 mm Hg (298 K)
- Vapor Density 4.5 times that of air
- Sorption coefficient (Koc) 160 (Kow=2.42)
- Liquid density 1.46 g/cm³
- Solubility 1,100 mg/l (298 K)
- Henry's constant 0.0103 (298 K)
- *EPA Reg. IX Soil PRG 0.053 mg/kg (res); 0.11 mg/kg (ind)*
- *EPA MCL = 5 ppb*



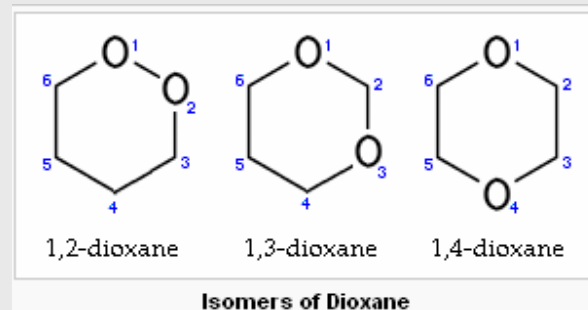
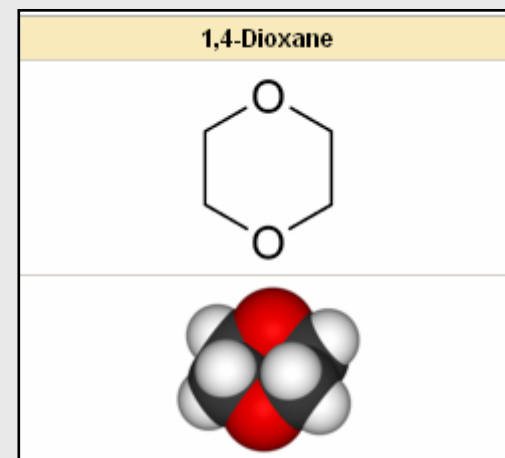
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CHEMICAL PROPERTIES

Dioxane

- TCE is unstable in the presence of metal over prolonged exposure, hence the need for a stabilizer.
- Dioxane ($C_4H_8O_2$) introduced as a stabilizing additive in the 1960s
- Vapor pressure 38 mm Hg (25°C)
- Kow 0.27
- Liquid density 1.033 g/cm³
- Solubility = completely miscible
- Henry's constant 3.88E-4
- Reportedly does not biodegrade in environment
- *EPA Reg. IX Soil PRG 44 mg/kg (residential); 160 mg/kg (industrial)*
- *California Action Level 3 ppb (currently no MCL)*



Wikipedia

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Laboratory Analytical Methods for Perchlorate Soil and Groundwater

DRINKING WATER

- ❖ U.S. EPA Method 314.0
- ❖ U.S. EPA Method 314.1
- ❖ U.S. EPA Method 331.0
- ❖ U.S. EPA Method 332.0

GROUNDWATER/SOIL

- ❖ SW 6850
- ❖ SW 6860
- ❖ Field Screening

FOOD, BOTTLED WATER, MILK

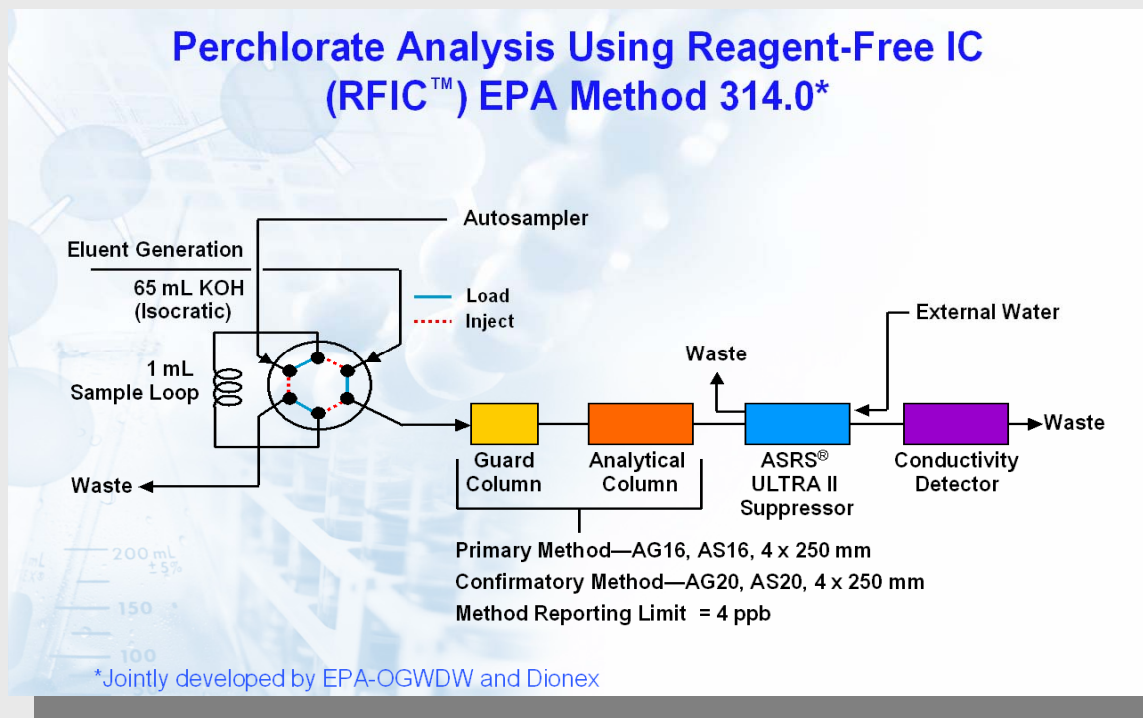
- ❖ FDA Method

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U.S. EPA Method 314.0 (IC):

- Category I interference: direct chromatographic coelution (poor QA/QC)
- Category II interference: concentration dependent coelution
 - Caused by high concentrations of anions (Cl^- , SO_4^{2-} , CO_3^{2-})
 - Lab must test maximum conductivity threshold
- Category III interference: overwhelm resin
 - high ionic strength (Ca^{2+} , Mg^{2+})

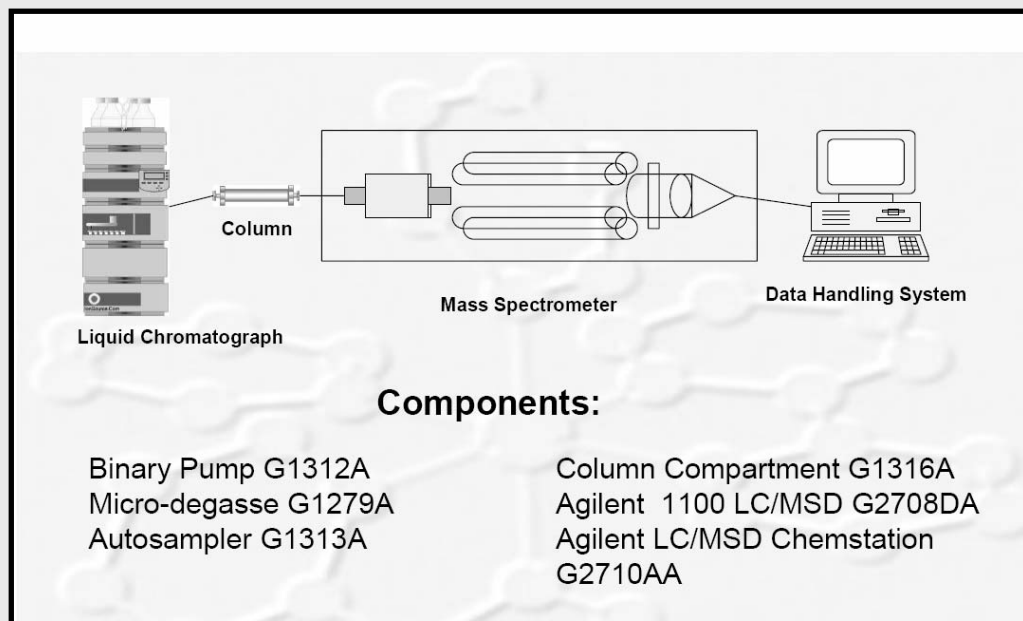


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Method 6850 (LC/MS)

- Potential hydrogen sulfate ion ($\text{H}^{34}\text{SO}_4^-$) interference ($m/z=99$)
 - Strip an oxygen, analyze at $m/z=83$ and $m/z=85$ (ratio in nature of 2.3 to 3.8)
 - Internal standard added at $m/z=89$ (^{18}O isotope)
- Shifted elution (early) if high competing anions (uptake on resin)
- Early elution of high TDS (Cl^- , SO_4^- , CO_3^- , etc) can interfere with perchlorate signal
- Water $0.2 \mu\text{g/l}$ MDL
- Soil $2.0 \mu\text{g/l}$ MDL



Slide from Data Chem Laboratories, Inc.

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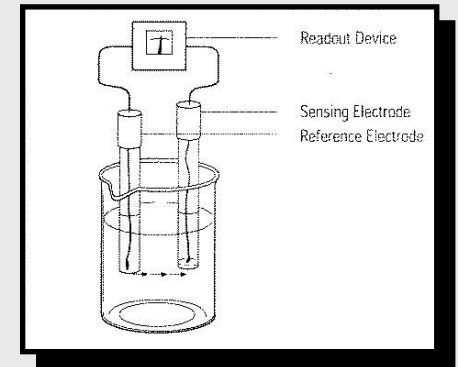
Comparison 314.0 to 6850 (Soil)

Sample ID	Depth	Perchlorate	Perchlorate
		314.0	DOD
	feet bgs	mg/kg (ppm)	mg/kg (ppm)
B-15-10	10	0.47	0.41
B-15-30	30	<0.02	0.018
B-15-40	40	<0.02	0.0067
B-15-50	50	<0.02	0.013
B-15-60	60	<0.02	0.0022
B-16-10	10	0.069	0.07
B-17-20	20	0.033	0.041
B-17-30	30	0.025	0.04
B-18-10	10	0.032	0.035
B-22-10	10	0.05	0.057

Field Screening...

Calibration

- Ion Selective Electrode (ESE)
- Reference Electrode
- Standard Preparation (Serial Dilution)
 - ♦ Perchloric Acid versus Potassium Perchlorate
 - ♦ 1 mg/l, 10 mg/l, 100 mg/l, and 1,000 mg/l
 - ♦ Direct Measurement (>1 mg/l; linear calibration)
 - ♦ Low Level Measurement (non-linear calibration)
 - ♦ Regression Analysis (Standard Curve)



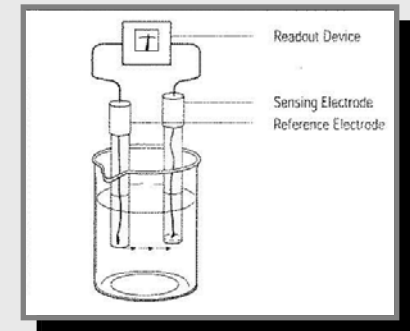
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Field Screening...

Measurement (Soil Samples)

- Soil Sample Preparation
- Perchlorate Extraction
- Decant and Filter (0.45 μm)
- Measure Perchlorate Concentration
- Controlling Interferences
 - ♦ *Ionic Strength Adjuster*
 - ♦ *Dilution*
 - ♦ *pH adjustment*
 - ♦ *Precipitation*



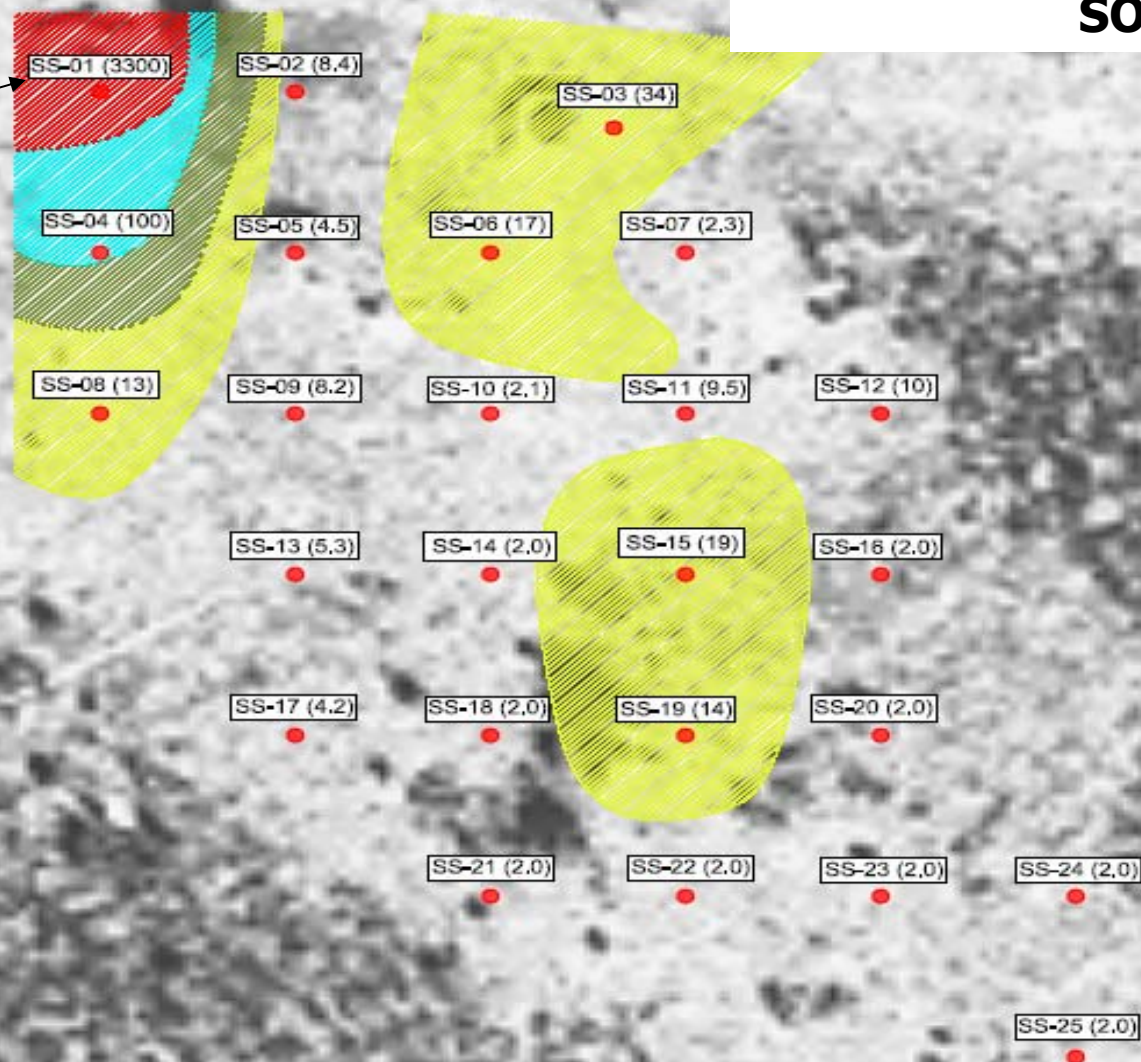
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SITE CONCEPTUAL MODEL

PERCHLORATE IN SURFACE SOIL

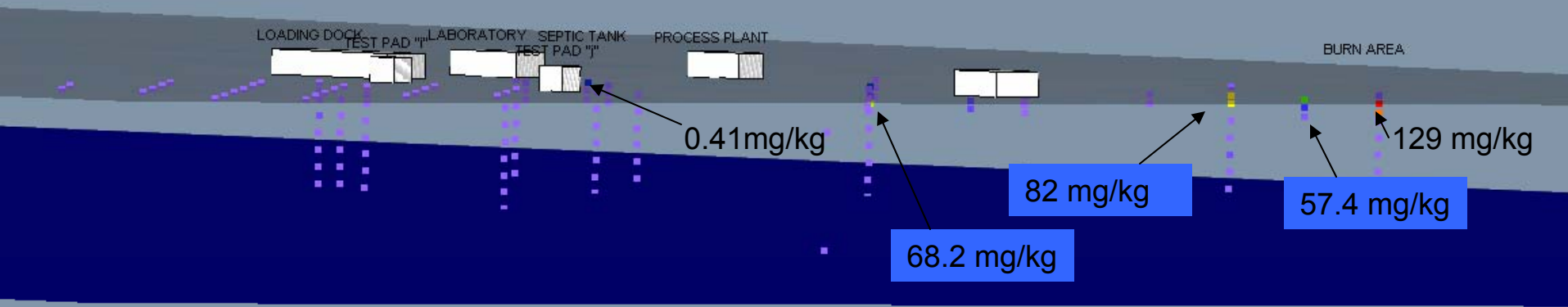
3.3 ppm



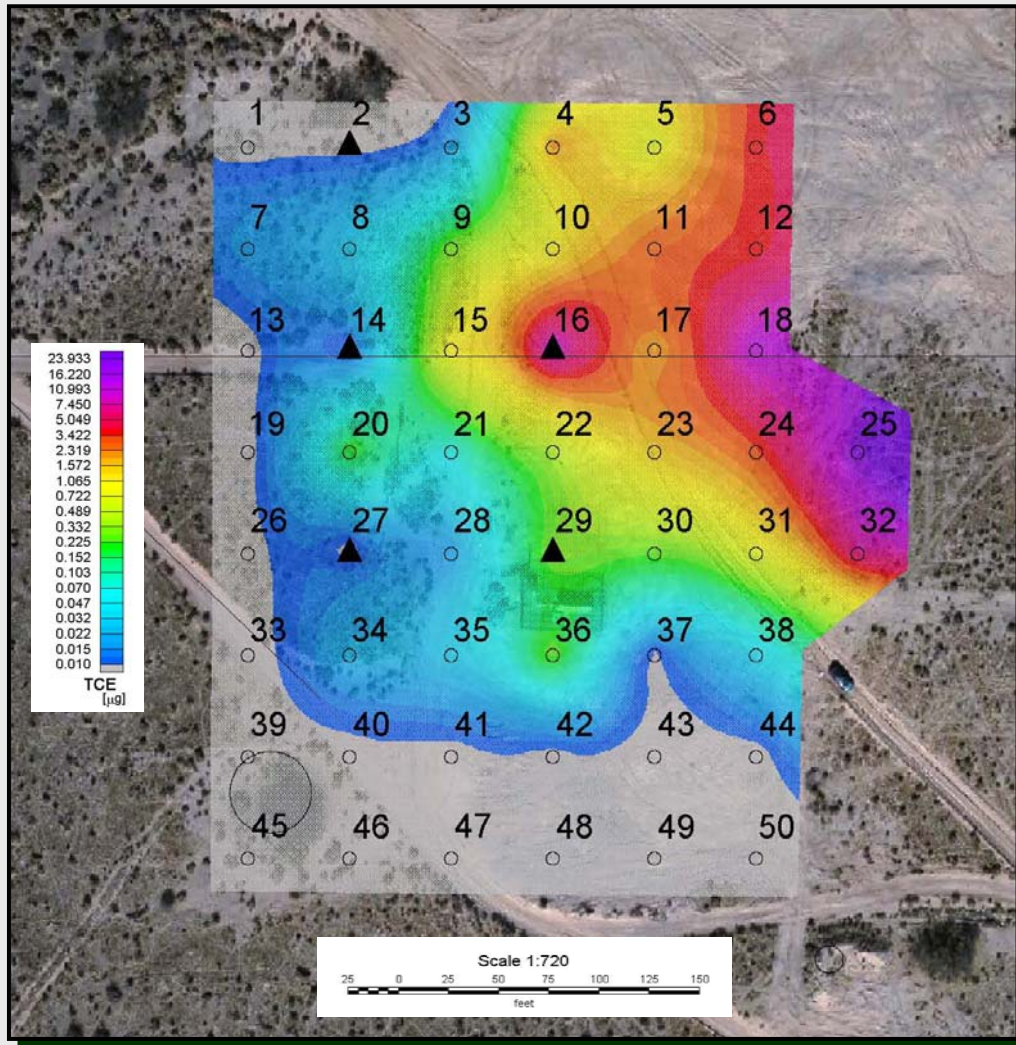


SITE CONCEPTUAL MODEL

PERCHLORATE IN SOIL



GORE MODULE SURVEY



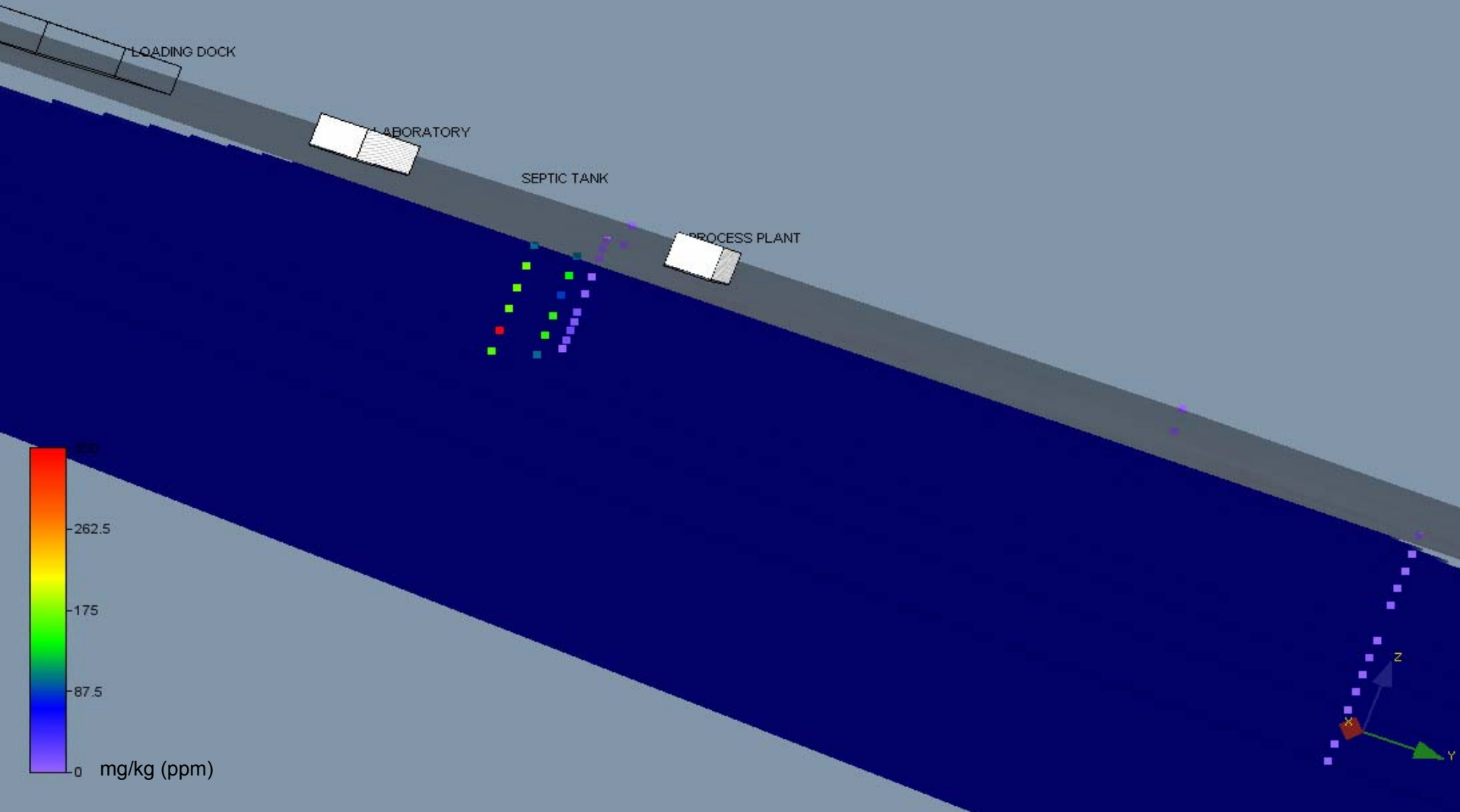
- 50 Sample Locations
- 50 Foot Spacing
- Analyze for VOCs (TCE)

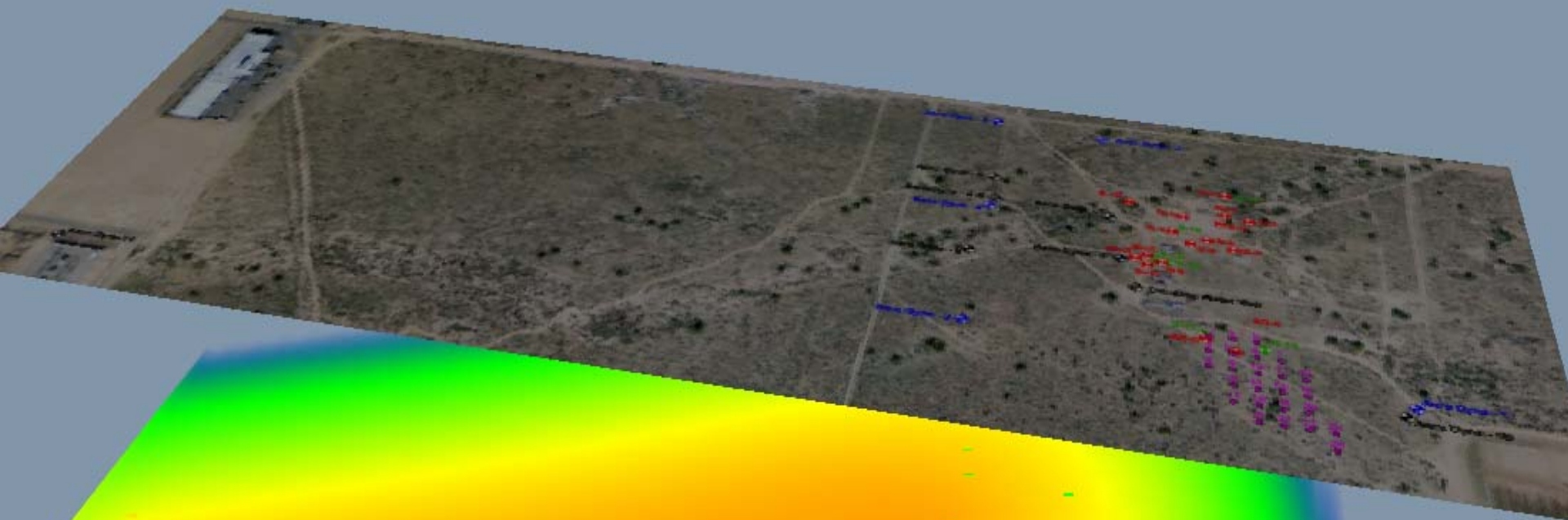
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SITE CONCEPTUAL MODEL

TCE IN SOIL





SITE CONCEPTUAL MODEL
PERCHLORATE IN GROUNDWATER
(SIMILAR TO TCE)



ADDITIONAL ASSESSMENT AND REMEDIAL APPROACH

- Data still being collected with regard to vertical and horizontal extent of perchlorate, TCE, and/or dioxane
- Remedial approach and/or risk assessment as necessary will ultimately reflect complete site conceptual model
- Look at scenario where remedial approach needed for all three primary contaminants of concern (i.e., perchlorate, TCE, and dioxane)

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REMEDICATION

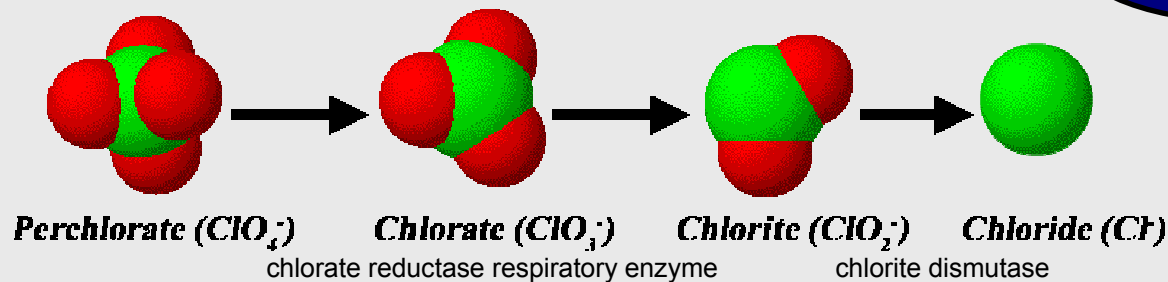
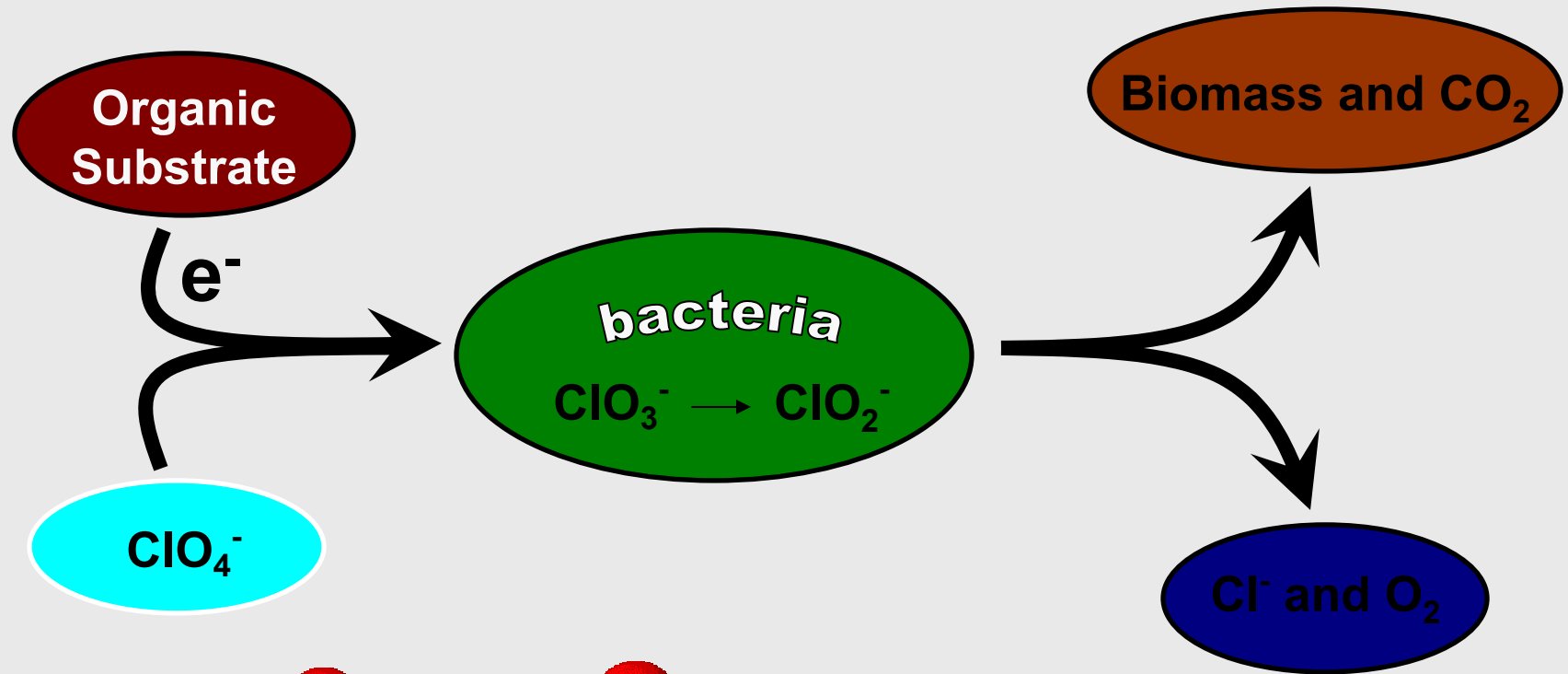
SOURCE AREA (SOIL)

- Shallow soil (≤ 20 -25 feet) may be excavated, or capped
- Vapor extraction for TCE and/or dioxane
- Evaluate donor injection for vadose zone (perchlorate and TCE).

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Biological Perchlorate Reduction



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Electron donors are environmentally innocuous



Ethanol



Citric Acid



Acetic Acid



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REMEDATION

DISSOLVED PLUME: DIOXANE

- Well suited to removal by groundwater extraction due to high solubility and low degree of partitioning to organic matter in soil
- Relatively low Henry's Constant makes technologies such as air stripping generally ineffective in treating the chemical in water
- Low adsorptive capacity also limits the effectiveness of treatment by granular activated carbon (GAC)

Source: EPA, December 2006

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REMEDATION

DISSOLVED PLUME: DIOXANE

- Use of hydroxyl radicals to sequentially oxidize organic contaminants to carbon dioxide, water, and residual chlorine (if chlorinated hydrocarbons are present)
- Various approaches:
 - Hydrogen peroxide with UV light ($\cdot\text{OH}$ generated in contaminated water with added H_2O_2) (electricity and peroxide costs can be significant)
 - Ozone with hydrogen peroxide ($\cdot\text{OH}$ generated through ozonation of contaminated water with added H_2O_2) (reduced electricity and peroxide costs. Ex. HiPOxTM systems).
 - Hydrogen peroxide with ferrous iron (i.e., Fenton's Reagent) (little research available for this approach with dioxane)
 - Ozone with UV Light (little research available for this approach with dioxane)

Source: EPA, December 2006

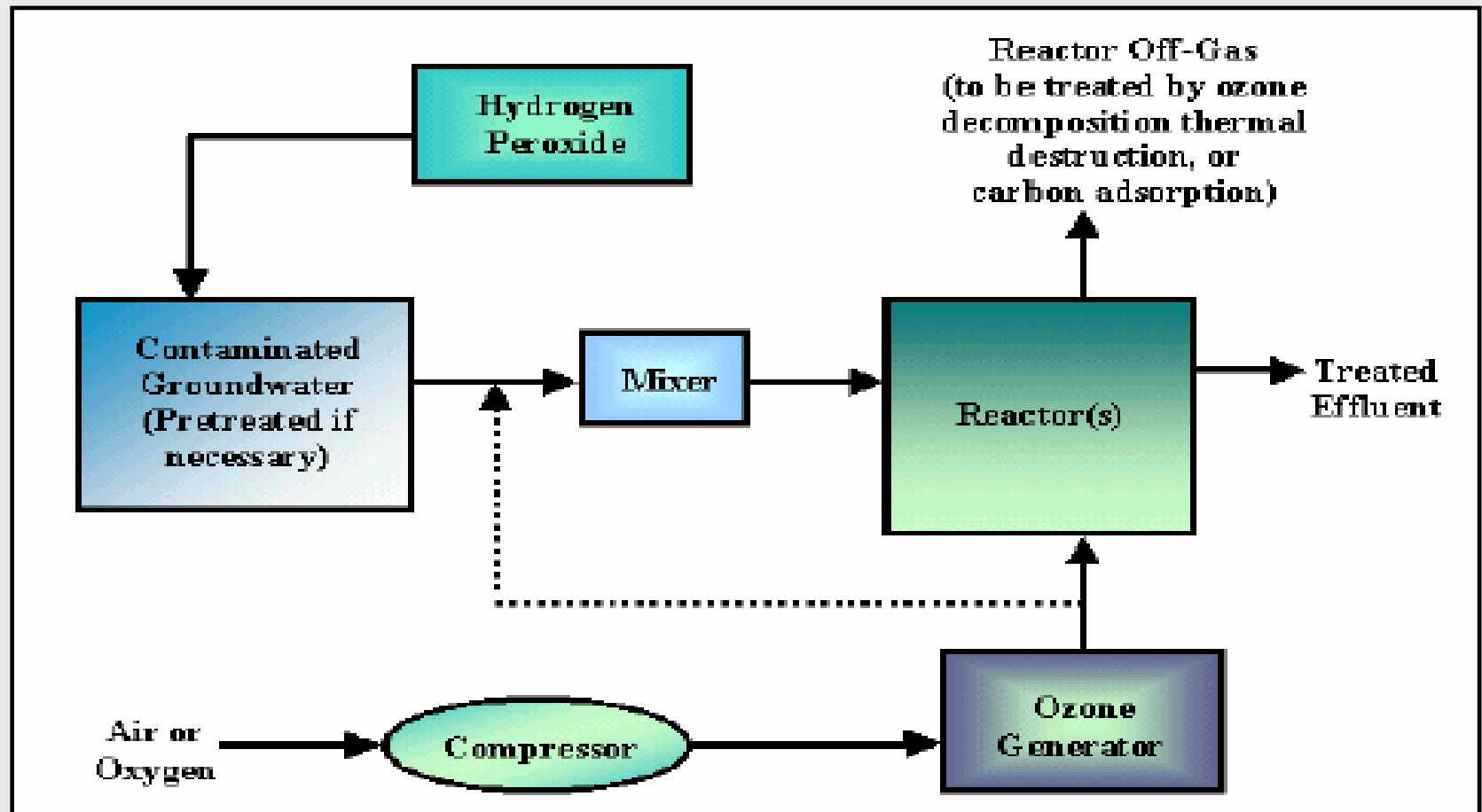
$\text{C}_4\text{H}_8\text{O}_2 + 20(\cdot\text{OH}) \rightarrow 4\text{CO}_2 + 14\text{H}_2\text{O}$ (H_2O_2 cost approx. \$0.85/lb). Less efficient with UV approach.

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REMEDIATION

DISSOLVED DIOXANE



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LOCATION	TYPE OF APPLICATION	FLOW RATE (gpm)	PROJECT TYPE	INFLUENT CONCENTRATION (µg/L)		EFFLUENT CONCENTRATIONS (µg/L)
San Gabriel, CA	Drinking Water	1,000	Full-Scale HiPOx installation	TCE PCE 1,2 DCE 1,1 DCE	604 697 28 25	36 174 ND ND
Sparks, NV	Remediation	40	Full-Scale HiPOx installation	MTBE	4,000	Discharge limit: 100 µg/L; HiPOx Effluent: <10 µg/L
San Gabriel, CA	Drinking Water	1,000	Full-Scale HiPOx installation	TCE PCE 1,2 DCE 1,1 DCE	604 697 28 25	36 174 ND (<0.5) ND
Newark, CA	Remediation	10	Full-Scale HiPOx installation	MTBE TBA TAME TPHg	100,000 8,500 9,400 24,000	ND (<5) ND (<5) ND (<10) ND (0.5)
South El Monte, CA	Remediation	1000	Full-Scale HiPOx installation	PCE TCE 1,2 DCE 1,4 -Dioxane MTBE 1,1 DCA	130 6 <0.5 5 <1 4	7 ND (<0.5) ND (<0.5) <2 <1 3.1
Tustin, CA	Remediation	70	Full-Scale HiPOx installation	MTBE	35,000	ND (<5)
South Lake Tahoe, CA	Drinking Water	800	Full-Scale HiPOx installation	MTBE	14	ND (<5)
City of Industry, CA	Remediation	70	Full-Scale HiPOx installation	1,4 Dioxane	470	<3
Turlock, CA	Remediation	10	Full-Scale HiPOx installation	MTBE TBA BTEX TPHg	278,000 51,000 60 450	ND (<5) ND (<10) ND ND
Beatty, OR	Remediation	25	HiPOx Cabinet Unit	1,4 Dioxane	200	<3
Turlock, CA	Remediation	5	HiPOx Cabinet Unit	MTBE TBA	9000 1000	ND (<5) ND (<10)
Las Vegas, NV	Remediation	5	HiPOx Cabinet Unit	MTBE TBA	3500 950	<0.5 <12

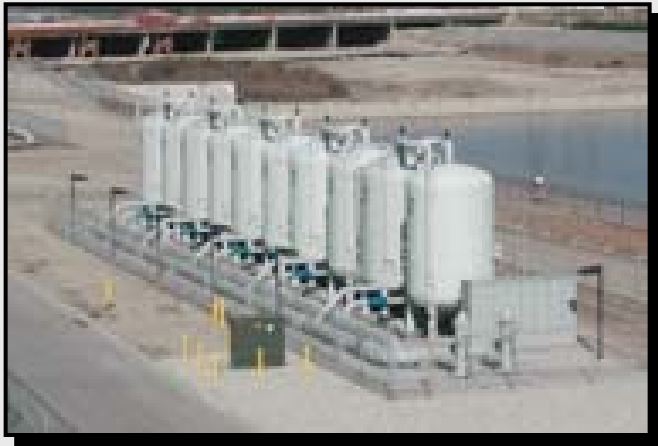
REMEDICATION DISSOLVED PLUME

- Ex-situ treatment requirement for dioxane (typical) suggests consider ex-situ treatment of TCE and perchlorate
- Consider ion exchange for perchlorate treatment (<50 µg/l)
- Consider combination air stripper and/or GAC for treatment/polishing of TCE

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REMEDIATION DISSOLVED PERCHLORATE



Picture from Calgon Corporation

- Perchlorate concentrations $<50 \mu\text{g/l}$, ion exchange cost effective
- Modular system minimizes capital cost and facilitates system delivery, installation, and startup
- Resin replacement by supplier
- Resin incineration with certificate of destruction mitigates perchlorate liability

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REMEDATION DISSOLVED PERCHLORATE

- Fixed Bed Ion Exchange Models:
 - Model 10 (1000 ft³; 1000 gpm)
 - Model 12 (1000 ft³; 2000 gpm)
- Ion Exchange Rental Option:
 - Mobilization: \$100,000
 - Initial resin: \$250,000
 - Monthly charge: \$3500 (either model)
 - Resin replacement: guarantee \$75/acre-foot (depending on concentration)
 - Demobilization: \$50,000
 - TOTAL COST (10 YRS, 250 gpm): **\$1,122,460**

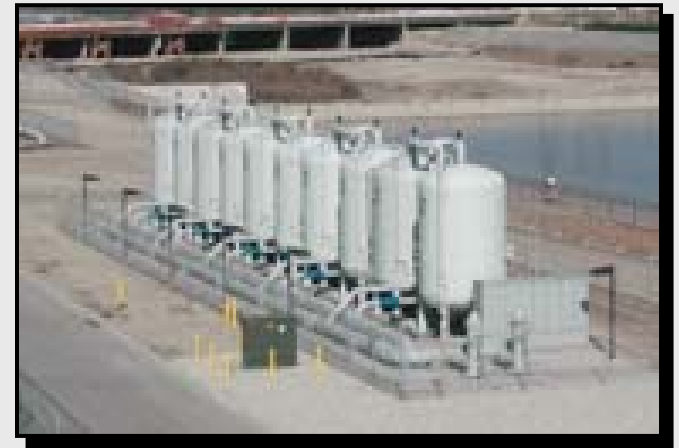


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REMEDATION DISSOLVED PERCHLORATE

- Fixed Bed Ion Exchange Models:
 - Model 10 (1000 ft³; 1000 gpm)
 - Model 12 (1000 ft³; 2000 gpm)
- Ion Exchange Purchase Option:
 - Mobilization: \$100,000
 - Model 10: \$500,000
 - Model 12: \$600,000
 - Demobilization: \$50,000
 - Resin replacement: guarantee \$75/acre-foot (depending on concentration)
 - TOTAL COST (10 YRS, 250 gpm): **\$1,052,460**



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REMEDICATION

DISSOLVED TCE

- Low TCE concentrations, consider use of HiPOxTM system
- With higher TCE concentrations, may require air stripper (will likely require thermal oxidizer) and/or GAC for treatment and/or polishing
 - Combination of H₂O₂, supplemental fuel, waste generation, and/or carbon changeouts can result in substantial operational costs

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REMEDICATION DISSOLVED PLUME

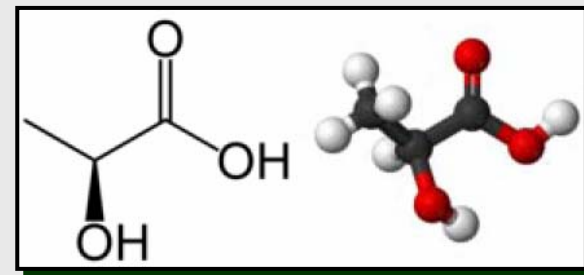
- Based on operational costs for Ex-Situ TCE treatment, consider alternative
- Consider in-situ donor sparging (TCE and perchlorate) with ex-situ oxidation (dioxane)
- Dioxane treatment is as previously described, but perchlorate/TCE treated in-situ upgradient of extraction wells for dioxane treatment

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REMEDICATION

DISSOLVED TCE

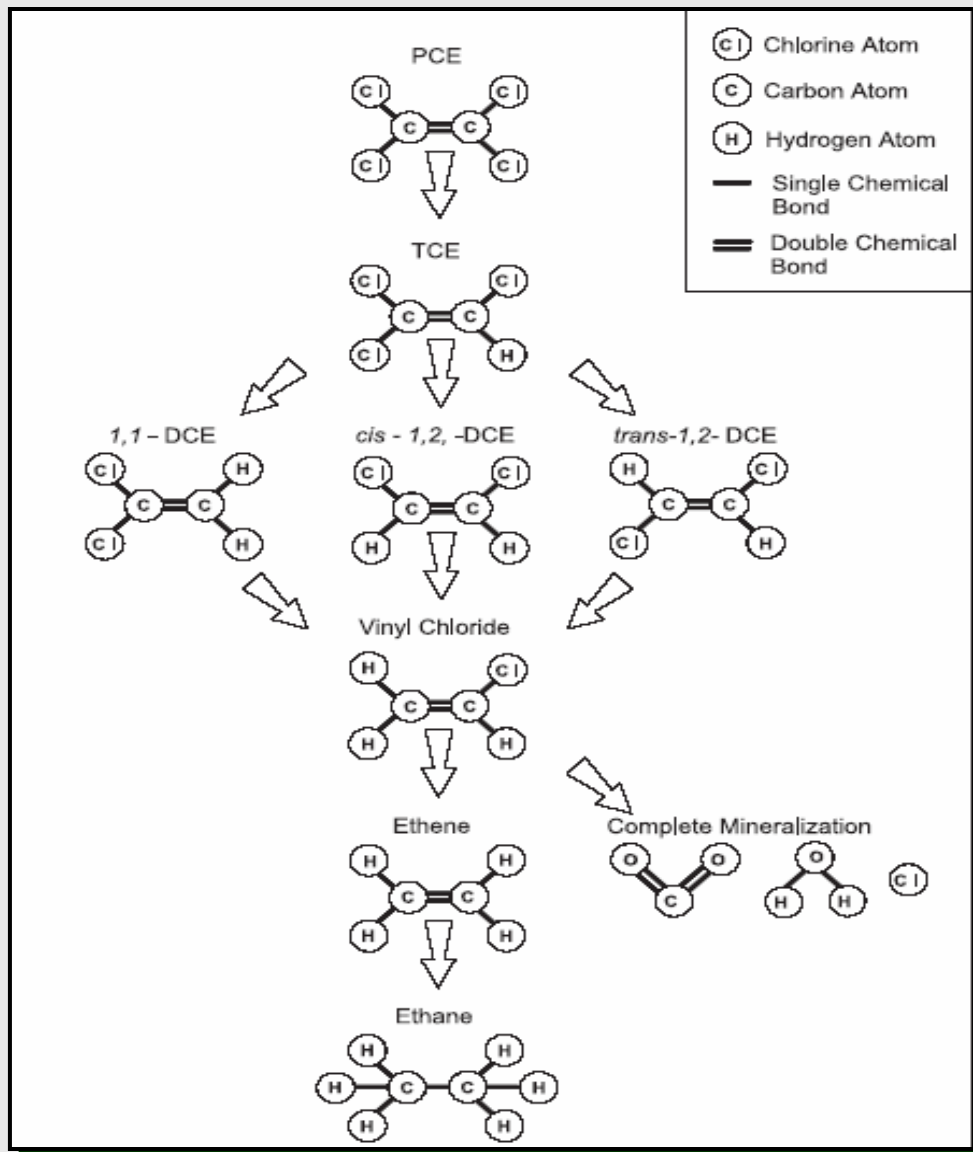


- Same electron donor may be capable of degrading perchlorate and TCE
- Example: Lactate electron donor. The hydrogen evolved from anaerobic fermentation of lactate and other substrates can also drive the reductive dehalogenation of chlorinated aliphatic compounds such as TCE
- Dehalococcoides (Dhc) enumeration:
ND (AD-7); 1×10^2 /l (AD-8); 8×10^2 /l (AD-6)
- Percent Dhc >0.01% (AD-6); >0.02% (AD-8) (as compared with KB-1 which has 50%)
- Results indicate low Dhc organism concentrations that are suboptimal for high rates of dechlorination
 - Use of electron donor to increase Dhc concentrations
 - Potential bioaugmentation (KB-1)

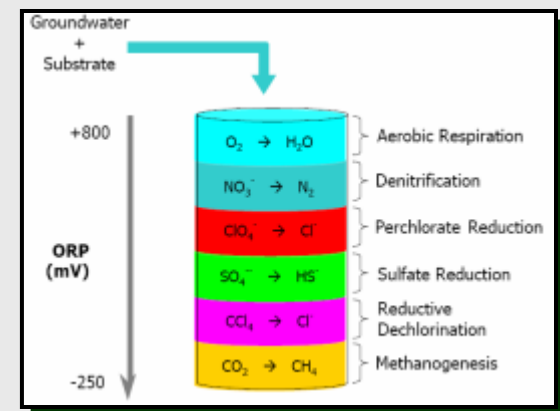
Source: Environmental Science and Technology, December 2001

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- Reductive dehalogenation of chlorinated ethenes



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CONCLUSIONS

- Still some work to do with regard to vertical and horizontal assessment of perchlorate, TCE, and dioxane.
- Perchlorate and TCE concentrations in soil documented above EPA Region IX PRGs. Some shallow excavation already completed.
- TCE in groundwater currently documented above MCL
- As necessary, soil remediation will include some combination of in-situ donor injection, excavation, and/or capping.
- As necessary, groundwater remediation will include some combination of ex-situ dioxane/TCE treatment utilizing advanced oxidation processes (AOP), and in-situ donor sparging for perchlorate and/or TCE.

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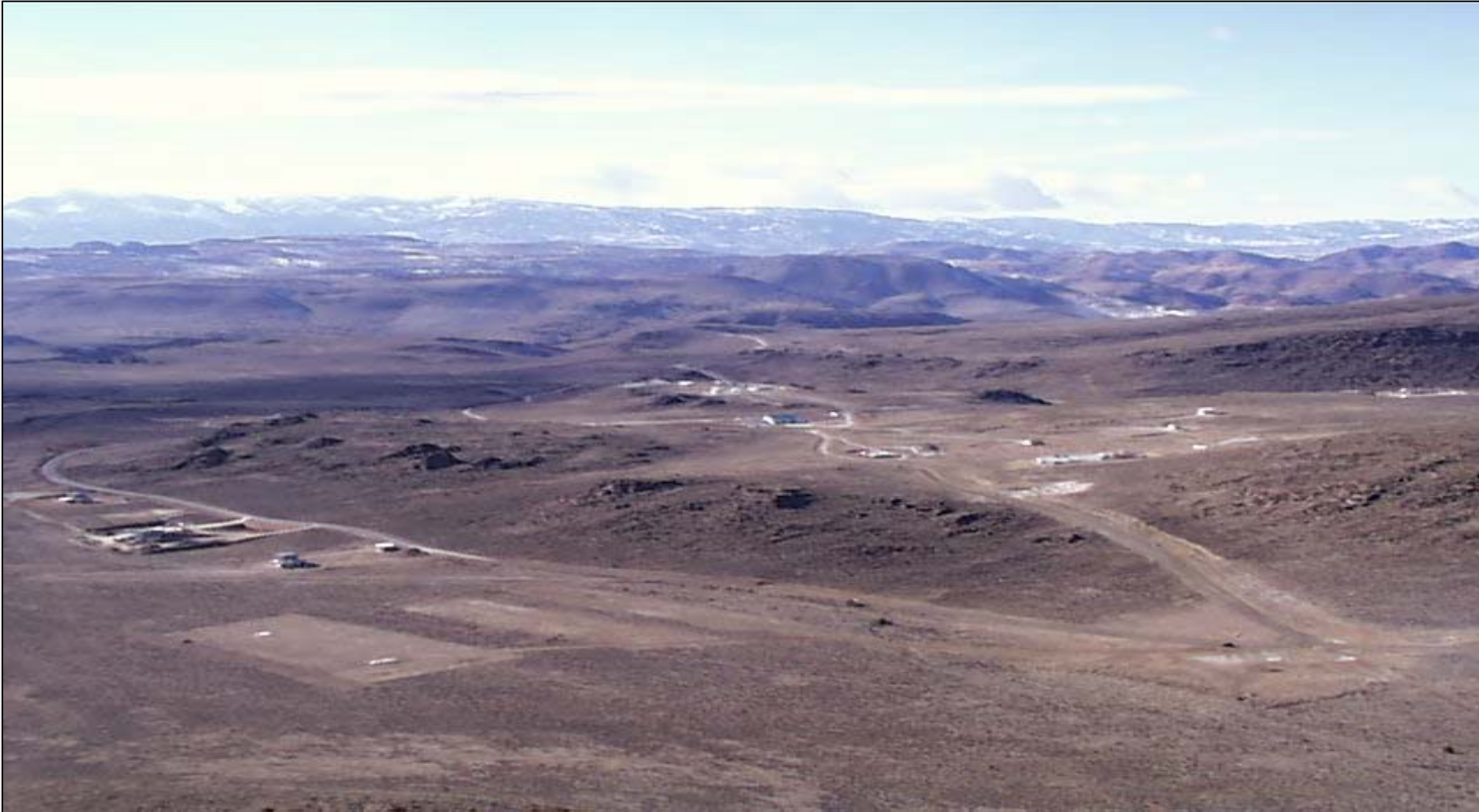
CASE STUDIES: Bioremediation of Perchlorate in Soil

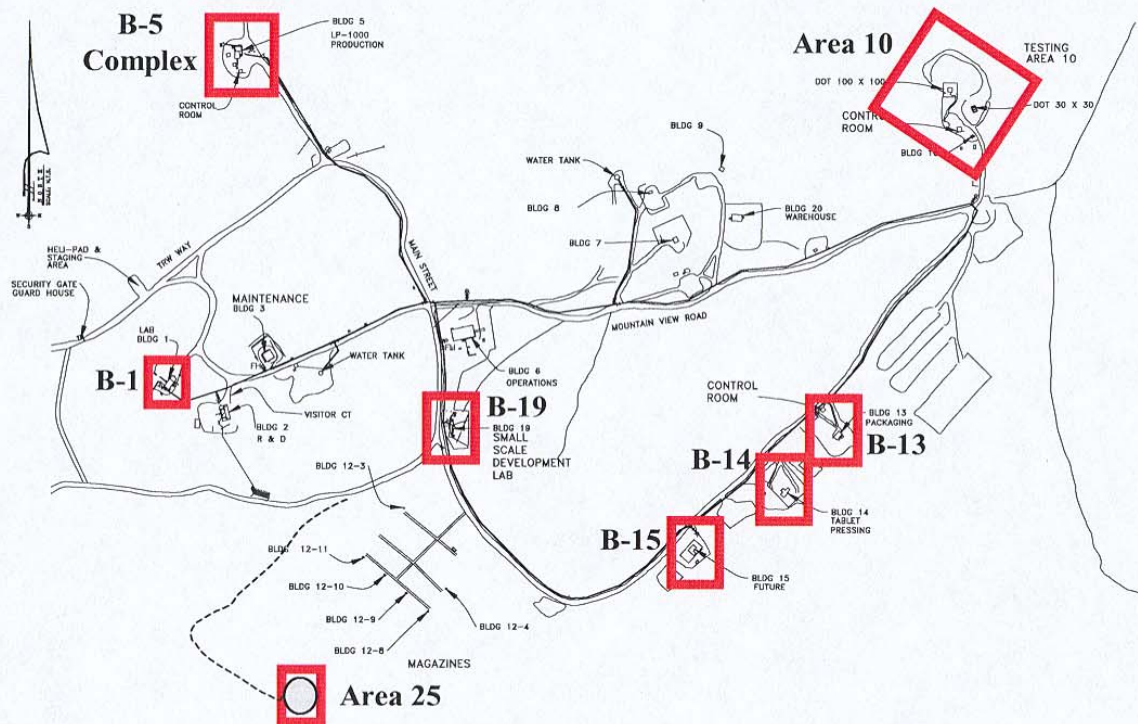


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Explosives manufacturing and testing site in Nevada





Approx 1.2 miles from well

Area 26

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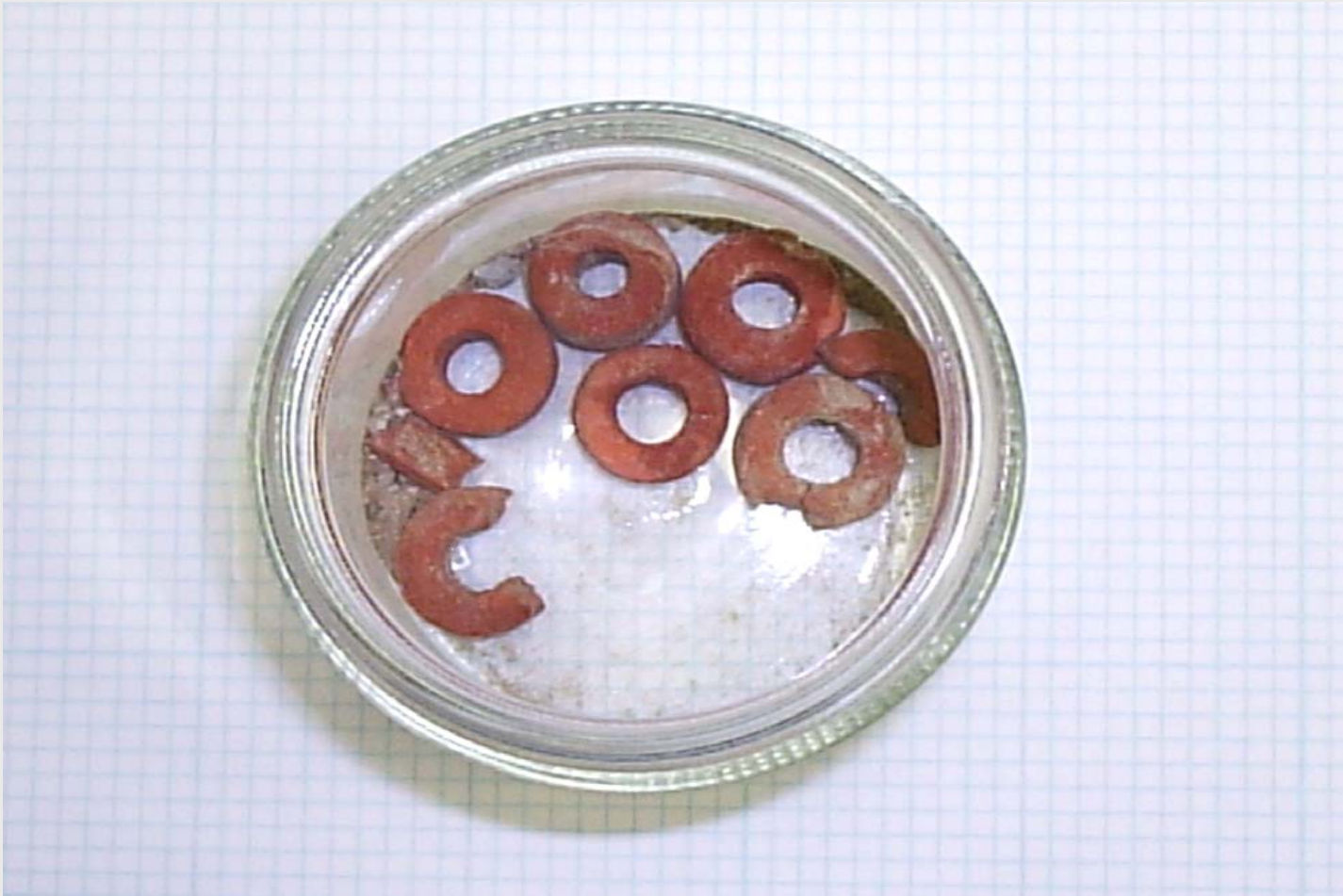
Damaged explosive monitoring post



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Propellant (PVAC) rings



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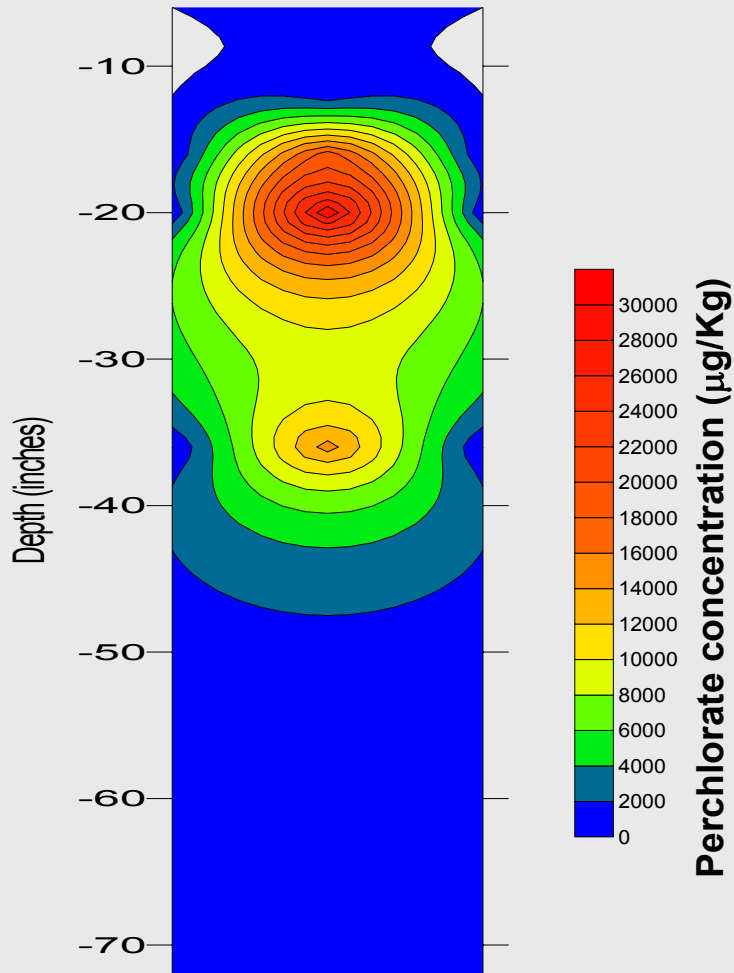
Area 10 Wood Bunker



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Perchlorate in soil at Wood Bunker

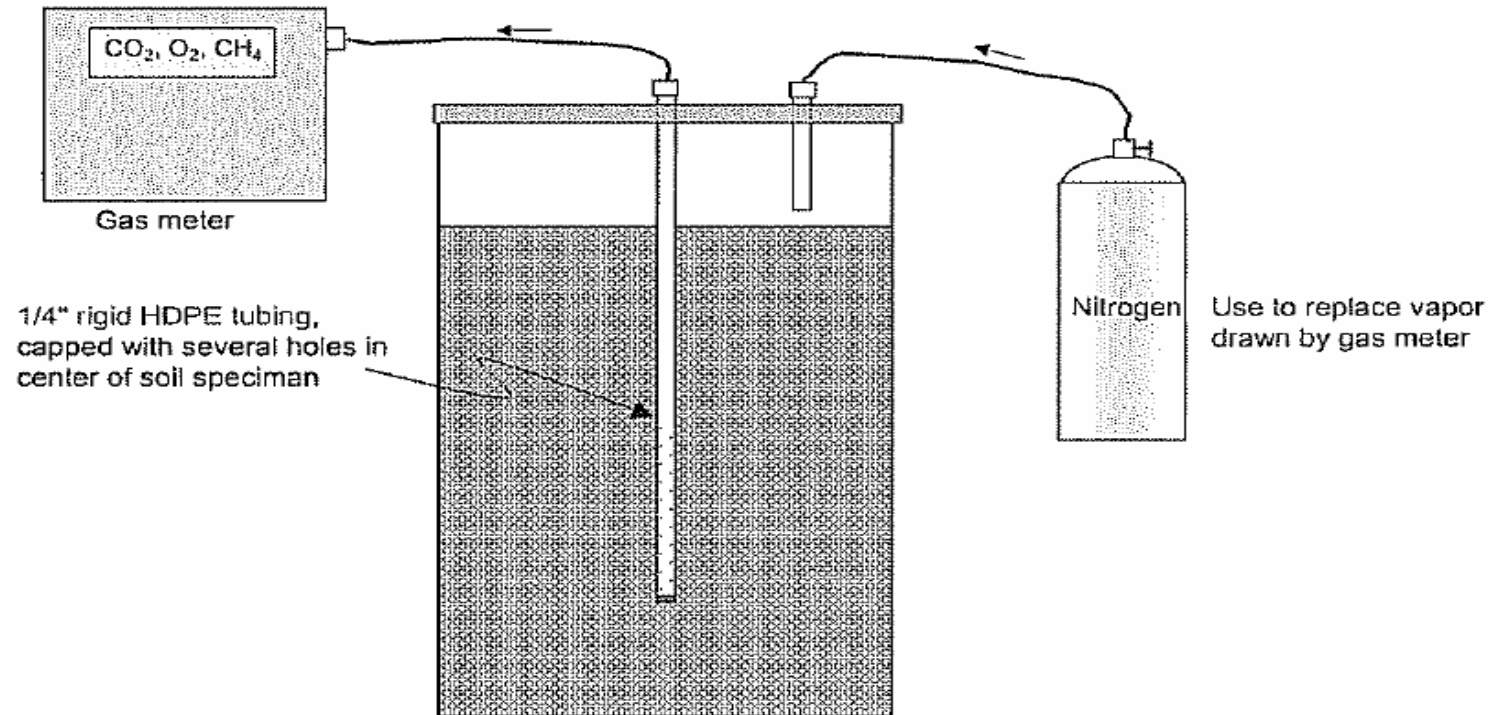


- ❖ Perchlorate mobile in sandy clay soil
- ❖ 630 $\mu\text{g/Kg}$ at 6 inches bgs
- ❖ 30,000 $\mu\text{g/Kg}$ at 30 inches bgs
- ❖ 353 $\mu\text{g/Kg}$ at 72 inches bgs

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Figure 1: Bench Scale Apparatus



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K L E I N F E L D E R

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Compost blending at Test Pad



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Molasses added and Test Pad covered



RESULTS

- ❖ Initial perchlorate concentration of 19,000 $\mu\text{g/Kg}$
- ❖ Final concentrations ranged from ND to 6,100 $\mu\text{g/Kg}$
- ❖ Concentration decrease ranged from 68% to 100%
- ❖ Perchlorate concentrations decreased below residential PRG of 7800 $\mu\text{g/Kg}$

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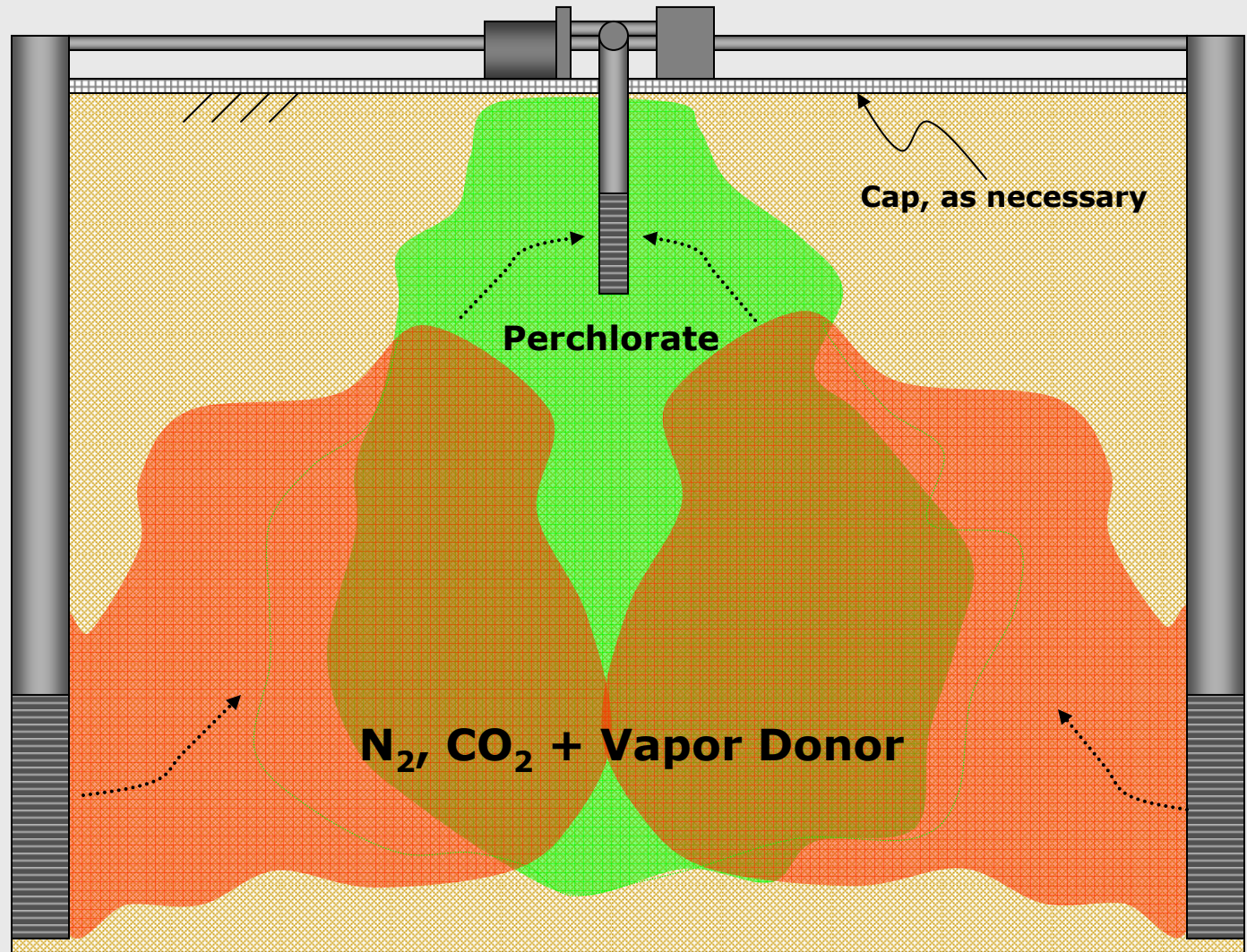
> EXPECT MORE

Potential In Situ Treatment for Deep Soil Contamination

A warm, moist mixture of carbon dioxide and nitrogen produced by an inexpensive flame generator is mixed with donor and injected into the subsurface.

The warm mixture rises while also being drawn upward through the source contamination by extraction well(s).

When stable, an extraction/injection loop is implemented between the wells to sustain degradation.



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CASE STUDIES:

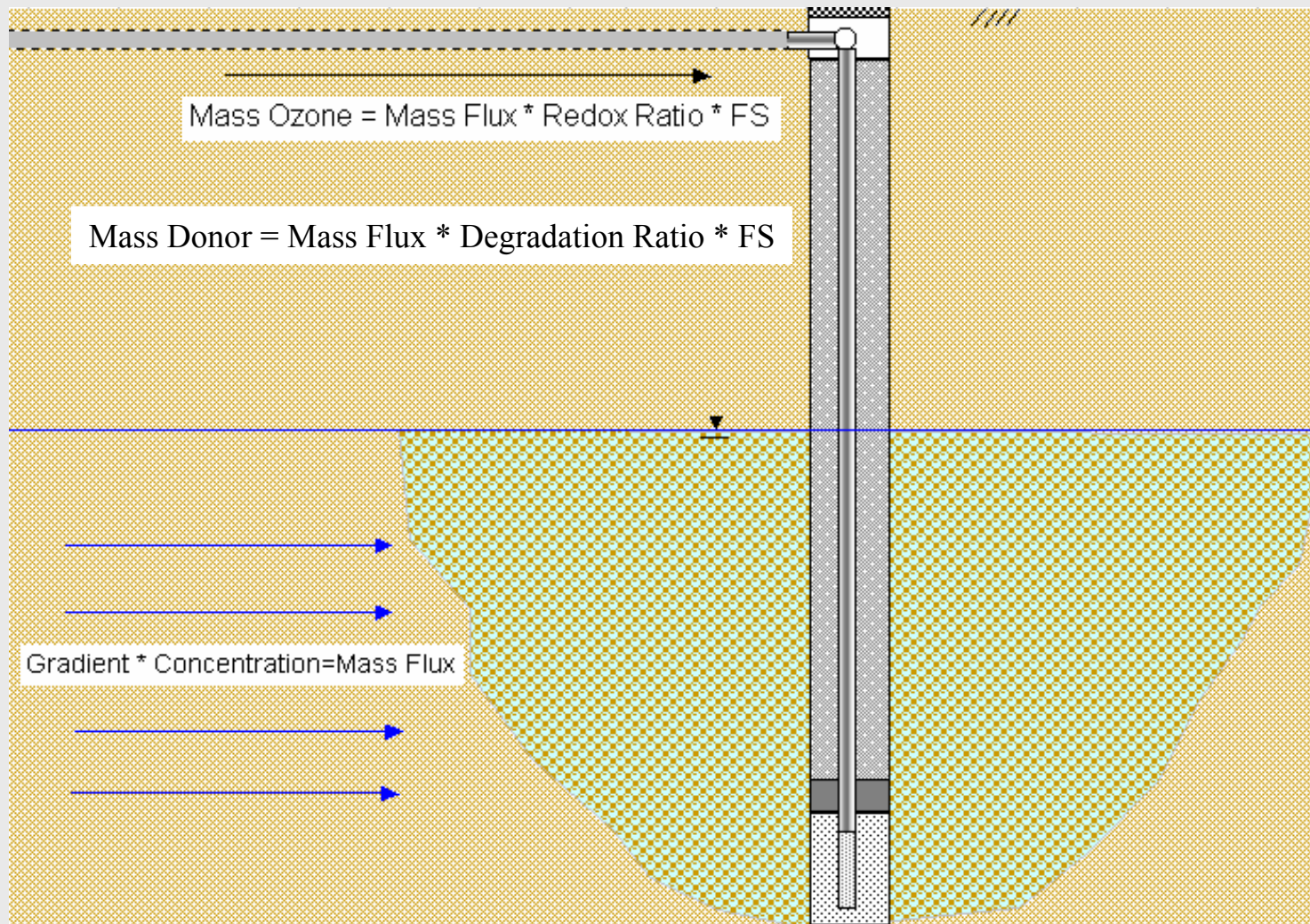
Bioremediation of Perchlorate in Groundwater



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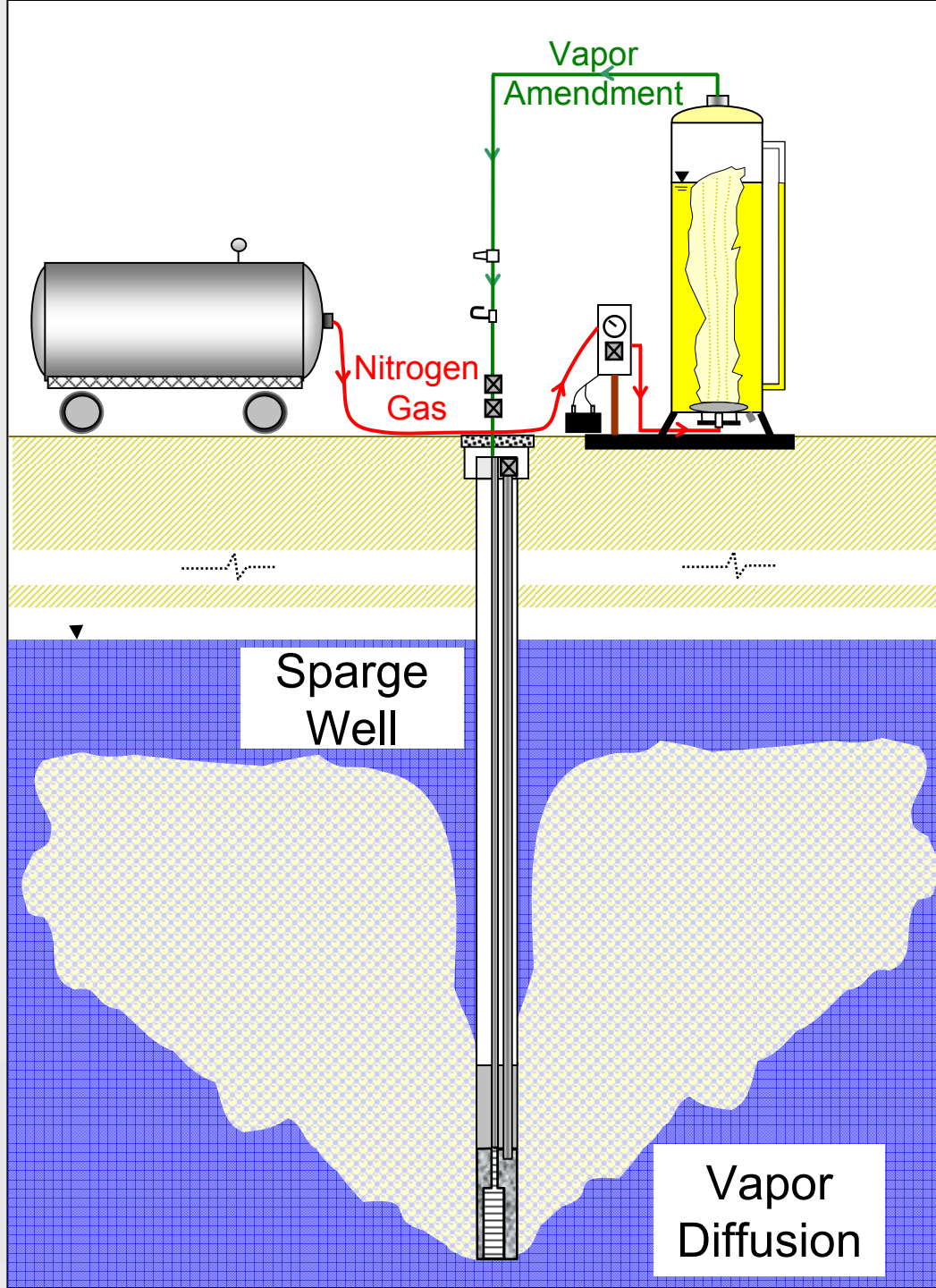
> EXPECT MORE

Approach to Engineering Plume Control

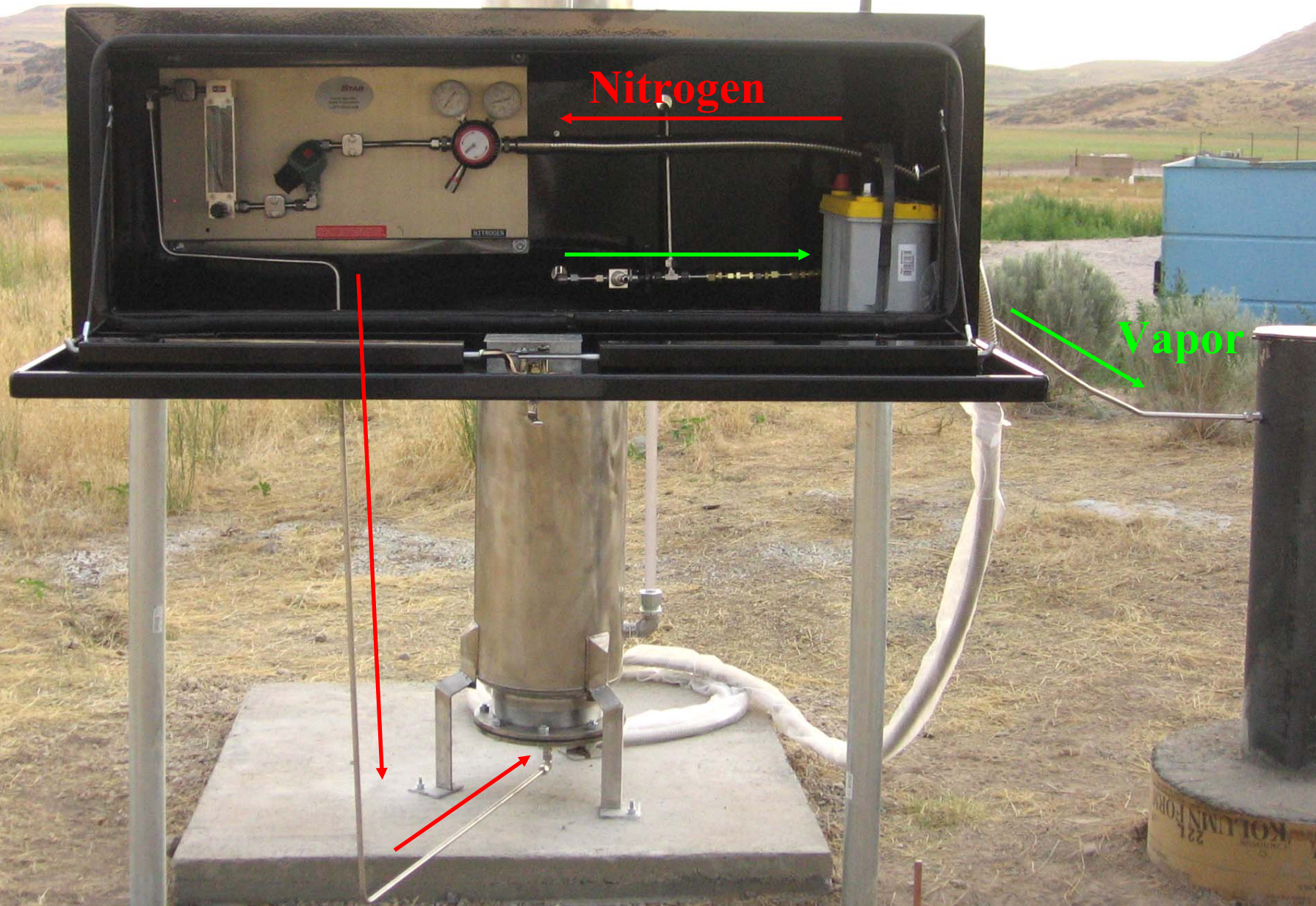


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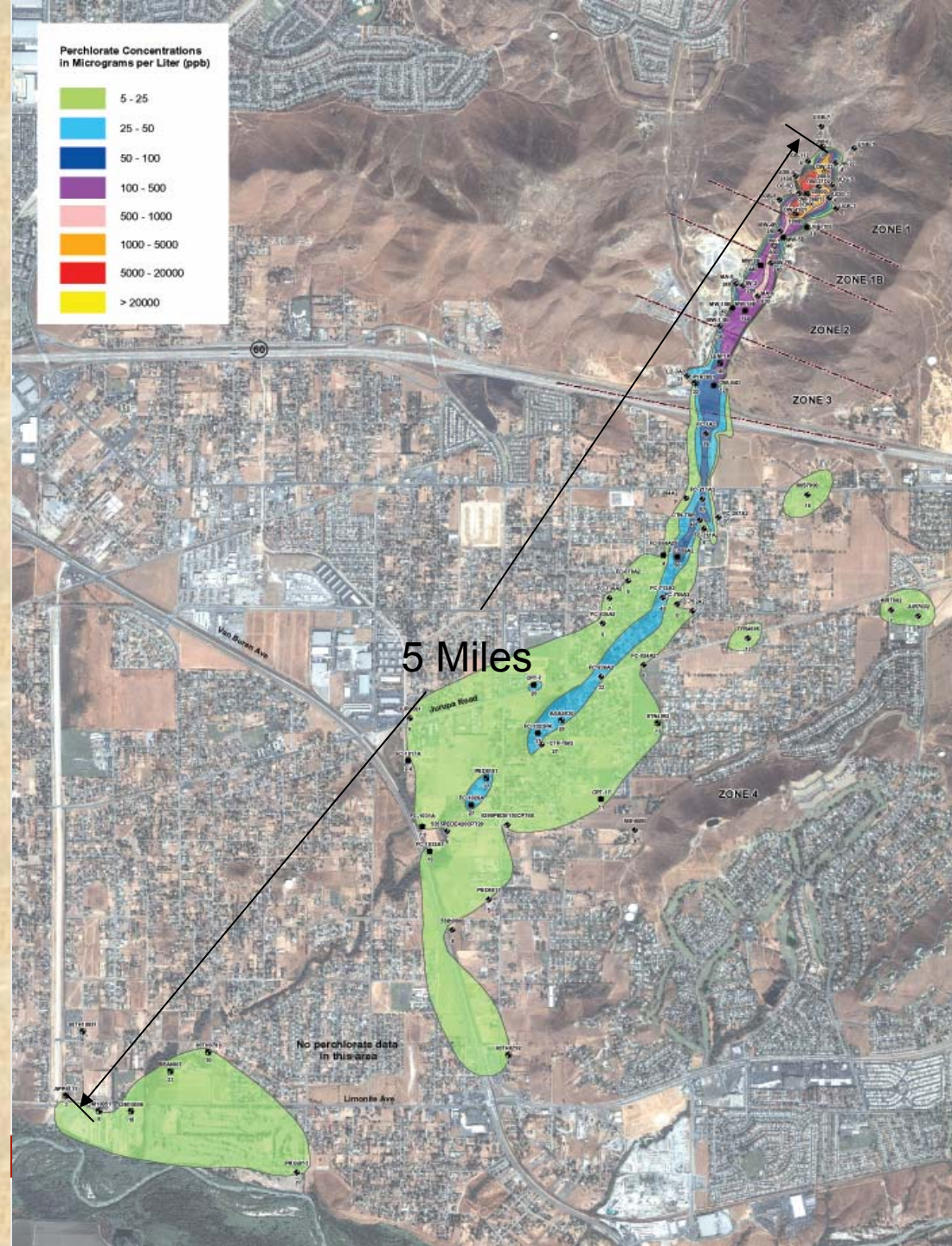


Nitrogen

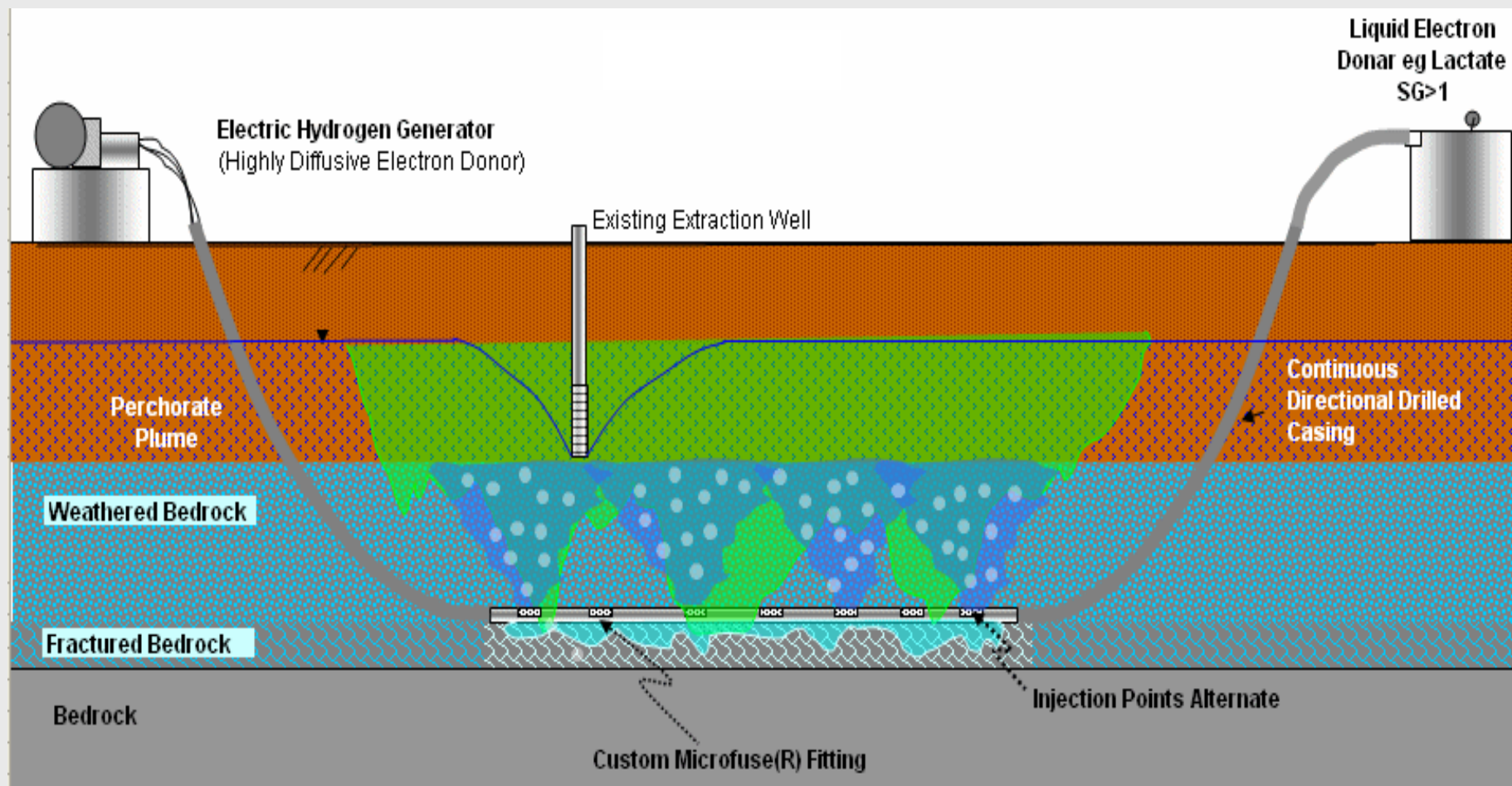
Vapor

Stringfellow Superfund Site

- Solvents and perchlorate
- Affects entire town
- Several secondary sources of perchlorate
- Suspected natural sources perchlorate
- Natural degradation at river boundary



Alternative Under Investigation for Stringfellow



Questions?

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